R&D of Energetic Ionic Liquids

Next Generation Energetic Materials – Striking a Balance between Performance, Insensitivity, and Environmental Sustainability

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14. ABSTRACT
Current research programs are aiming to develop ionic liquids (ILs) as energetic materials for various applications. Such applications for ILs include both propulsion and explosives. Within the propulsion arena, a focus is to replace hydrazine (a highly toxic compound) as a fuel. The approach to replacing hydrazine is the synthesis and development of ILs with substantially less vapor toxicity and superior energy density. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. The feasibility that an IL can undergo hypergolic ignition with a common oxidizer like nitric acid was demonstrated for the first time in our laboratory a few years ago (see references 1 and 2, below). Hazardous characteristics, undesirable physical and chemical properties of such ILs must be identified before further development by a potential user. IL-based fuels and their properties will be discussed (including limited safety and sensitivity, and thermophysical properties). 1. S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau and G. Drake, Energy Fuels, 2008, 22, 2871-2872. 2. S.D. Chambreau, S. Schneider, M. Rosander, T. Hawkins, C.J. Gallegos, M.F. Pastewait and G.L. Vaghjiani, J. Phys. Chem. A, 2008, 112, 7816-7824.

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RESEARCH AND DEVELOPMENT OF ENERGETIC IONIC LIQUIDS

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Current research programs are aiming to develop ionic liquids (ILs) as energetic materials for various applications. Such applications for ILs include both propulsion and explosives. Within the propulsion arena, a focus is to replace hydrazine (a highly toxic compound) as a fuel. The approach to replacing hydrazine is the synthesis and development of ILs with substantially less vapor toxicity and superior energy density. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. The feasibility that an IL can undergo hypergolic ignition with a common oxidizer like nitric acid was demonstrated for the first time in our laboratory a few years ago (see references 1 and 2, below). Hazardous characteristics, undesirable physical and chemical properties of such ILs must be identified before further development by a potential user. IL-based fuels and their properties will be discussed (including limited safety and sensitivity, and thermophysical properties).

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Performance/Environmental/Safety Challenge

Hydrazines are SOTA spacecraft fuel:

- **Increased Operations Costs:**
  - Carcinogenic Vapor (Respiratory Route)
  - Dermal Toxicity
  - Strong Reducing Agent
  - Flammable (LEL = 4.7%, UEL = 100%)
- **On-Orbit Propulsion Systems Affected**

System	Mission
FltSatCom	Communications
STARDUST	Deep Space Probe
INTELSAT	Communications
HEAO-B	X-Ray Astronomy

- **Hundreds of Satellites Use Hydrazine for RCS & ACS**

Advanced Chemical Propulsion For Spacecraft

Communication (Iridium)

Global Positioning & Navigation (NAVSTAR GPS)

Weather (NASA TRMM)

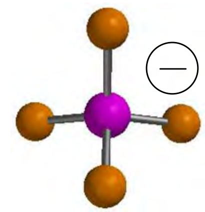
Spacecraft /Satellite propulsion employ hydrazines in both monopropellants and bipropellants

<u>Reduced toxicity can give</u>:
- lower handling cost
- lower transport cost
- more rapid response

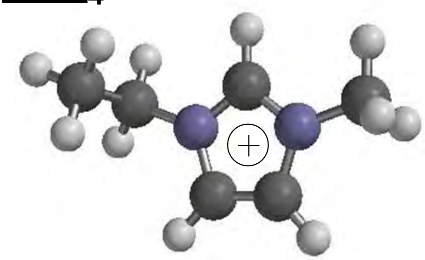
<u>Higher performance gives</u>:
- longer lifetime
- faster response time
- larger payloads

Energetic Ionic Liquids
Avenues to Lower Toxicity & Higher Performance

- **History**
  - An ionic compound that has a melting point at or below 100ºC
  - Seminal work at USAFA (Wilkes et.al.)
  - Industrial solvents, green chemistry
    - Low vapor pressure, low vapor toxicity
    - Wide solubility ranges

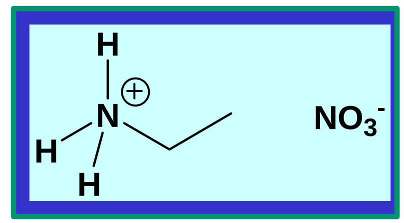


$AlCl_4^-$



EMIM cation
(1-ethyl-3-methylimidazolium)

- **ILs as *Energetic* Materials**
  - First energetic ILs: chemical oddities
  - AFRL realizes chemical structure manipulation leads to new classes of highly, energy dense materials (HEDM) for advanced propulsion



Liquid propellants:
Spacecraft thrusters
DACS/ACS
Booster engines

‘Greener’ Chemical Propulsion- ILs in Advanced Monopropellants

ADN (M.P. 92^{o}C) is also an Energetic Ionic Liquid

- ADN-based monopropellant (LMP-103S) from ECAPS, Swedish Space Corporation
- High performance ‘green’ propellant (30% Improved Isp*Density vs. hydrazine)
- 1 N Thruster using thermal and catalytic ignition flight qualified and flown (PRISMA)

AF-M315E is US Air Force IL-Based Monopropellant

- Significant physical property and performance advantages (50% improved Isp*Density)
- Ongoing hardware developments

Constituents	Weight %
ADN	60-65
Methanol	15-20
Ammonia	3-6
H_2O	balance

* Sjoberg et.al., Insensitive Munitions & Energetic Materials Technology Symp. Proc.,Tucson, USA, May 11-14, 2009

Properties	LMP-103S	AF-M315E	Hydrazine
Isp_{vac},lbf sec/lbm (e = 50:1 Pc = 300 psi)	252 (theor.) 235 (del)	266 (theor.) ~ 250 (del)	242 (theor.)
Density , g/cc	1.24	1.465	1.01
Vapor Pressure (torr)	Ammonia Methanol H_2O	<0.1 (w/o H_2O)	14.3

* Hawkins et.al., Proc. 4th International Association for the Advancement of Space Safety, Huntsville AL, 19 May 2010; Hawkins et.al., Proc. Fourth International Conference on Green Propellants for Space Propulsion, Noordwijk, The Netherlands, 20-22 June 2001.

Toxicity Assessment of AF-M315E

Toxicity Testing Results

- Time consuming
- Expensive

PROPERTY	AF-M315E	HYDRAZINE
LD50 (rat), mg/kg	550	60
Dermal Irritation (rabbit)	None - Slight	Corrosive
Dermal Sensitization (guinea pig)	Non Sensitizer	-
Genotoxicity (Ames)	3 Negative/2 Positive	Positive

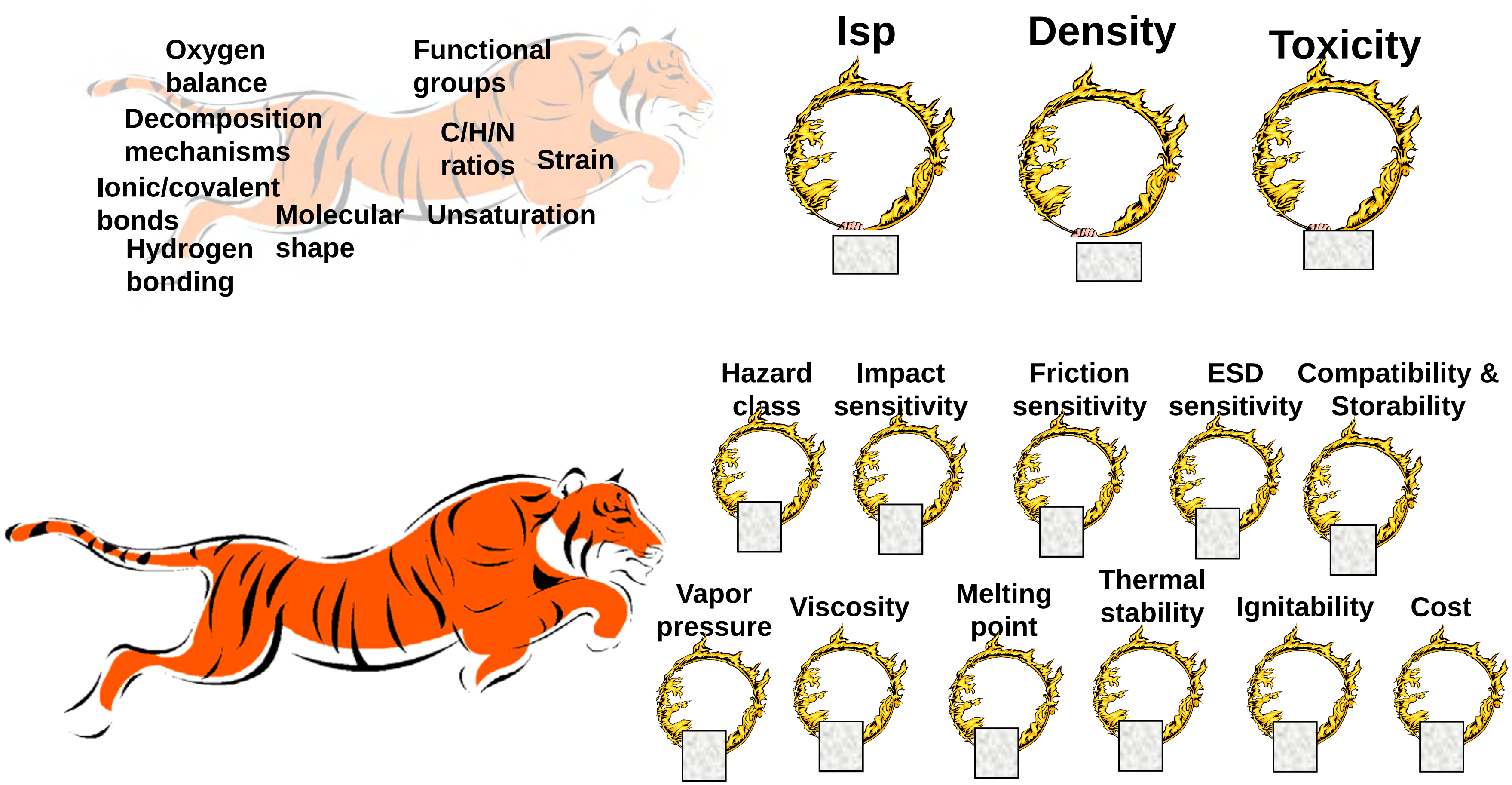
- Low hazard
- Low cost

Toxic Vapor ComponentsTesting

NASA White Sands Test Facility –No chemical species detected in the propellant headspace that are identified as carcinogens or have regulated vapor concentration limits (detection limit 2-3 ppb)

Propellant *Development*

There is more to it than performance & toxicity



Much Effort Required in Small-Scale Safety/Hazard Evaluations

Propellant	AF-M315E*	LMP-103S**
Unconfined Burn	Test 1 and 3: No reaction Test 2: burn	Negative (burn)
Drop Weight Impact Sensitivity (JANNAF Test Method)	126 Kg-cm (E_{50}) Lot 32 Reference material: N-Propyl Nitrate (21 kg-cm)	Under US Evaluation
Sliding Friction (Julius Peters –BAM)	352 N (5 consecutive “no go”) Lot 32	Under US Evaluation
TGA (75^{o}C/48 hours)	0.86 Wt % Excluding Volatiles	Under US Evaluation
Critical Diameter	4 in< Dc<7 in , Confined	~ 0.4 in (10 mm) , Confined
Electrostatic Discharge	>1J	Under US Evaluation

•Hawkins et.al., 4th International Association for the Advancement of Space Safety, Huntsville AL, 19 May 2010; Hawkins et.al., Proc. Fourth International Conference on Green Propellants for Space Propulsion, Noordwijk, The Netherlands, 20-22 June 2001.
**M. Nagamachi et.al., J.Aero.Technology and Management, V. 1, n. 2, Jul. - Dec. 2009; K. Anflo et.al., AIAA 2006-5212 42nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, 9 - 12 July 2006, Sacramento, CA.

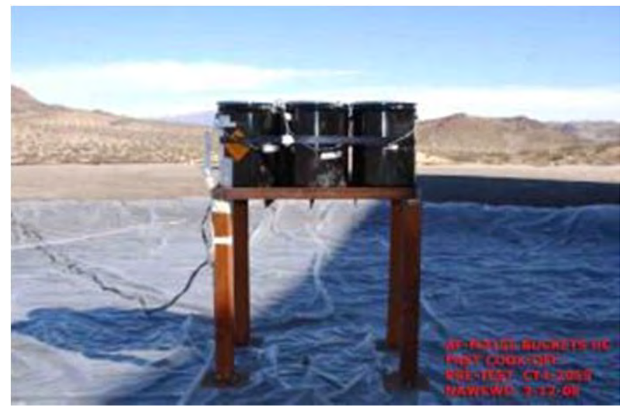
Even More Effort Required for Large-Scale Safety/Hazard Properties

Transition of AF-M315E to Aerospace Industry Requires a Final Hazard Classification (FHC)

Approved FHC Test Plan

- ***External Fire Test***
  - ➢ **Six 5-gallon composite pails**
- ***Sympathetic Detonation***
  - ➢ **5-gallon container in 20 gallon overpacks**
  - ➢ **Initiation method consisted of a ¼ lb C-4 booster on the container**

External Fire Test



External Fire and Stack Test Results

External Fire Test

- Propellant pails popped their lids and then individually burned mildly 6-8 minutes into the test
- All propellant and inner poly bottles were consumed
- No fragments thrown
- Thermocouples measured the flame temperature up to 1428°F

Mild burning reaction!

Unconfined PackageTest

No detonation/No burn- Passes test!

US DOT Granted Allowance For Two Package Configurations of AF-M315E

U.N. PROPER SHIPPING NAME AND NUMBER:

Propellant, liquid, UN0495

- **5 gallon composite container- 55 lbs of propellant in a 20 gallon drum over-pack (EX2010060551)**

Liquid Engine Alternative Propulsion Development Program (LEAP-DP)

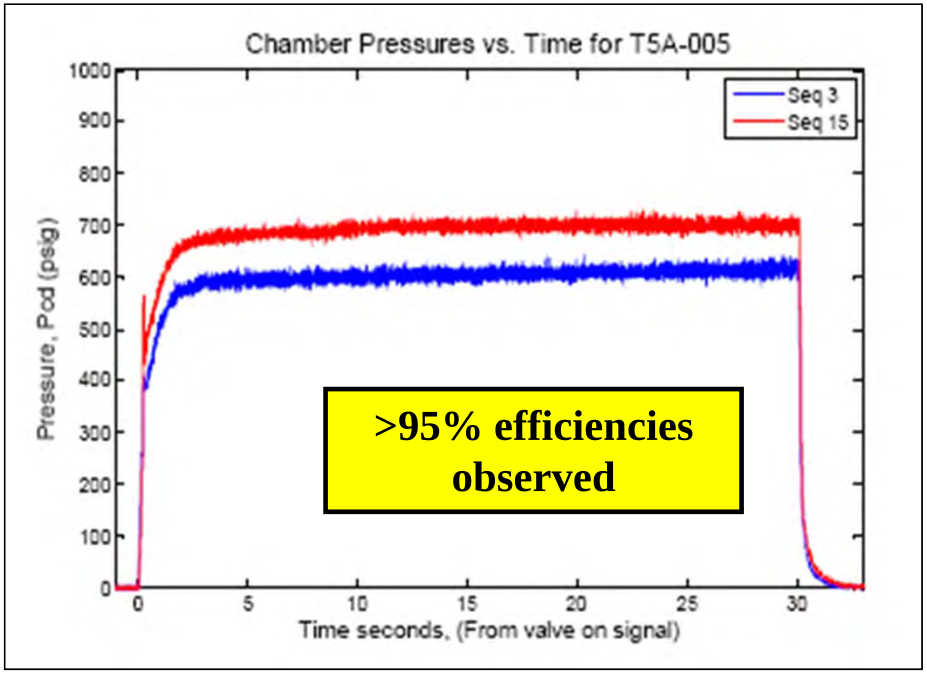
Technology Development

- **Demonstrate a survivable thruster to meet IHPRPT Phase II spacecraft monopropellant goal:** ***50% increase in Isp*ρ over hydrazine***
- **AFRL sponsored program performed by Gencorp Aerojet , Redmond WA, USA**

Achievements

- **High temperature catalysts and chamber materials capable of withstanding combustion temperature**
- **Good ignition response times**
- **Stable combustion - good chamber pressure roughness**

4.5 lbf Brassboard Thruster Pulses



Future work to concentrate on conversion from heavy weight to flight weight hardware

Ionic Liquids as Bipropellant Fuels

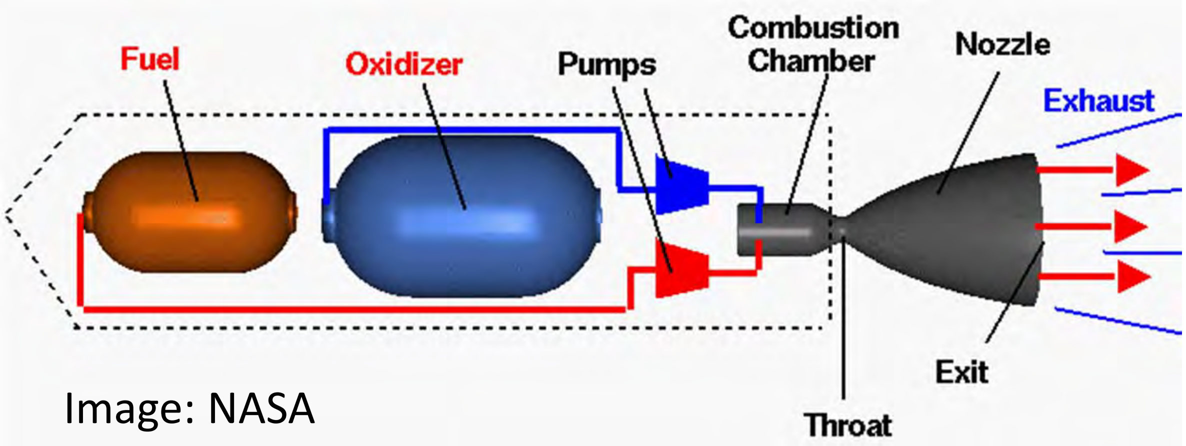


Image: NASA

- ❑ **Ignites**
- ❑ **Ignites Fast (10ms)**
- ❑ **Ignites Fast & Green(er)**

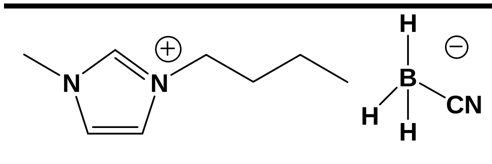
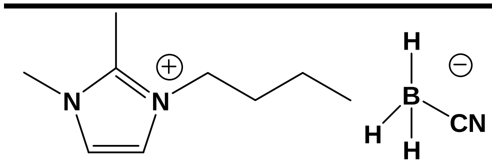
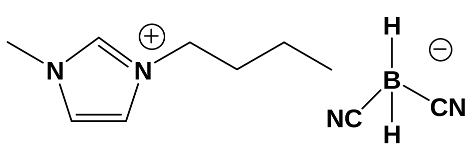
High Performance Ionic Liquid Fuels: Harnessing Metal Hydride Anions

Do Stable, Room Temperature Borohydride-Based ILs Exist that are Hypergolic to all Known Liquid Oxidizers (including the '*Greenest' Oxidizer* Hydrogen Peroxide)?

We know that solutions of LiAl hydrides and $LiBH_4$ in organic solvents are hypergolic with H_2O_2.

a) T.L. Pourpoint, J.J. Rusek, *5th International Hydrogen Peroxide Propulsion Conference*, Purdue University, West Lafayette, IN, September **2002**.
b) J.J. Rusek, *Proceedings of the 2nd International Conference on Green Propellants for Space Propulsion* (ESA SP-557), Sardinia, Italy June **2004**;

"The GREEN Flame"
Initial Borohydride-Based ILs

	Cyanoborohydride Ionic Liquid Fuels	Ignition delay[m]	Decomp. Onset [°C]
*		11	146
		600	249
**		28	307

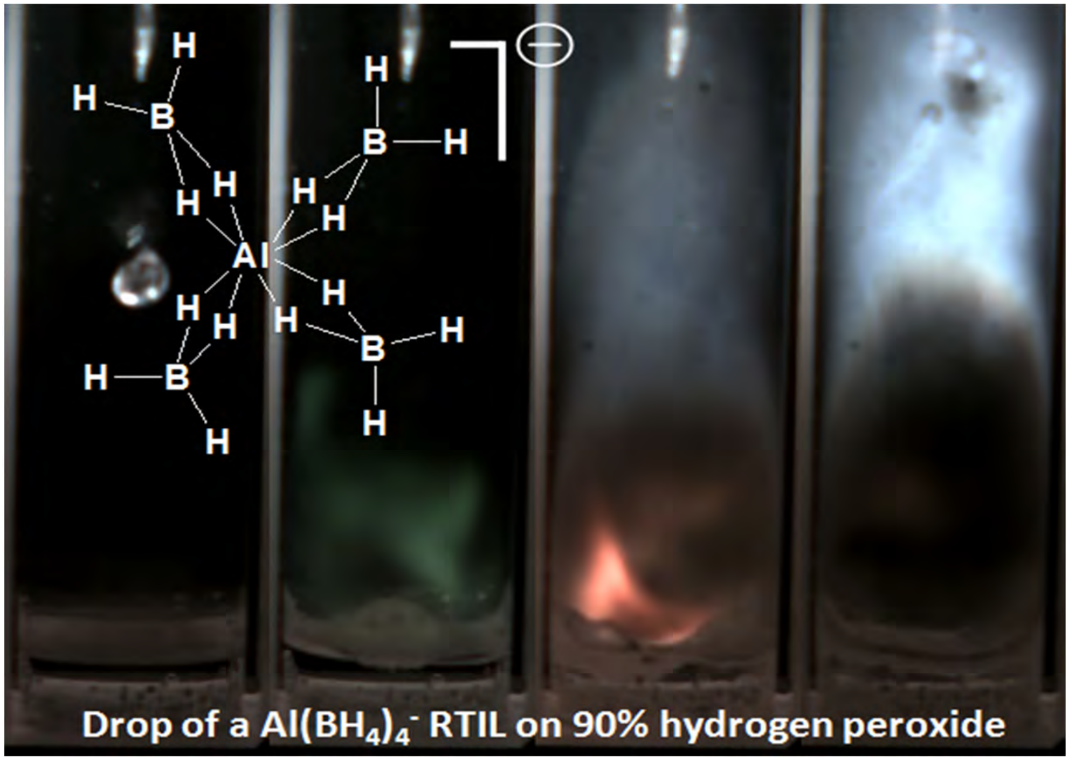
Demonstrated hypergolic with nitric acid-
But not with **N_2O_4 or H_2O_2**

- ❑ **Remarkable impact of cation (and anion) structure on reactivity/stability**

* **T. Hawkins, S. Schneider, L. Hudgens, M. Rosander Invention Disclosure, "Environmentally enhanced hypergolic ionic liquids" , Feb 4, 2010; Provisional Patent Application, June 17, 2010.**

** **Y. Zhang, J. M. Shreeve, *Angew. Chem.* 2011, *123*, 965-967; *Angew. Chem. Int. Ed.* 2011, *50*, 935-937.**

A Stable, Room Temperature IL Fuel Based on Borohydride Anion: $[Al(BH_4)_4]^-$



Drop of a $Al(BH_4)_4^-$ RTIL on 90% hydrogen peroxide

- **trihexyl-tetradecyl-phosphonium (THTDP) cation known to be stable with bases and reducing agents***
- **THTDP known to reduce melt point and promote liquidus**
- **$[Al(BH_4)_4]^-$ also promotes liquidus**

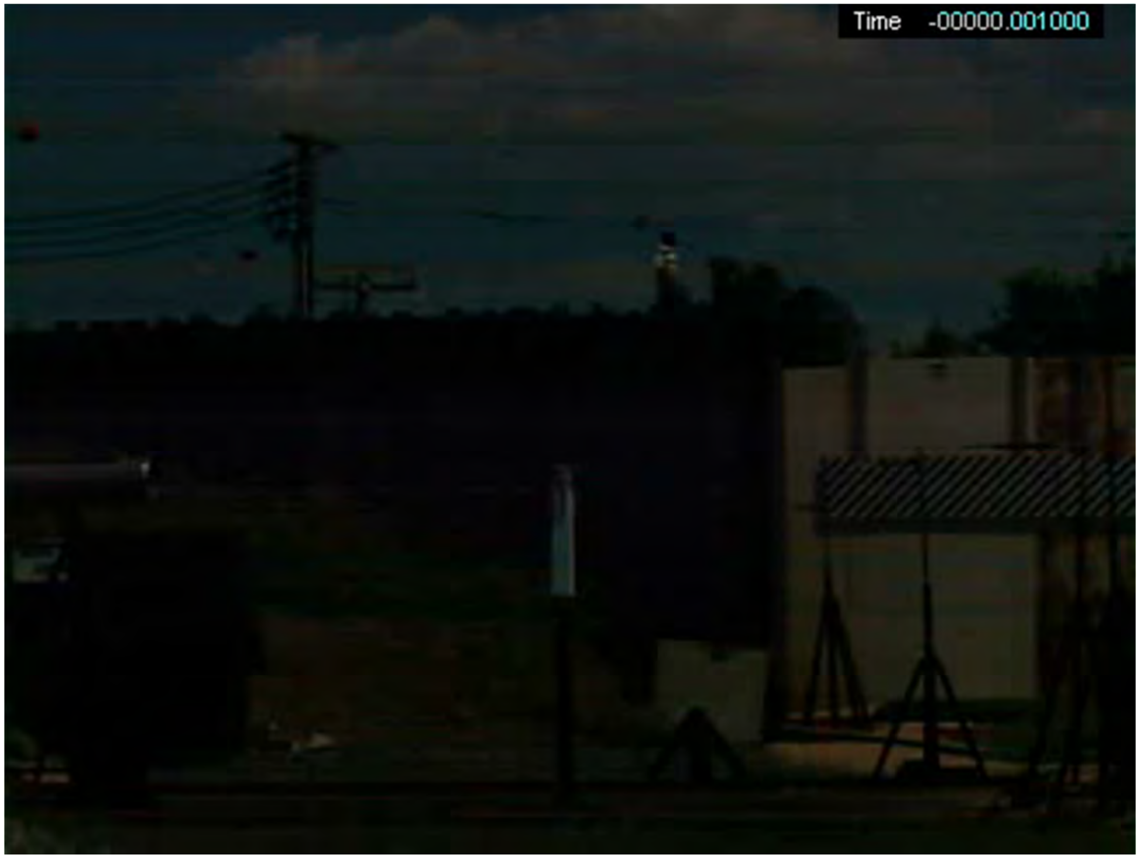
Combined, the two ions create a low viscosity, hypergolic IL-fuel!

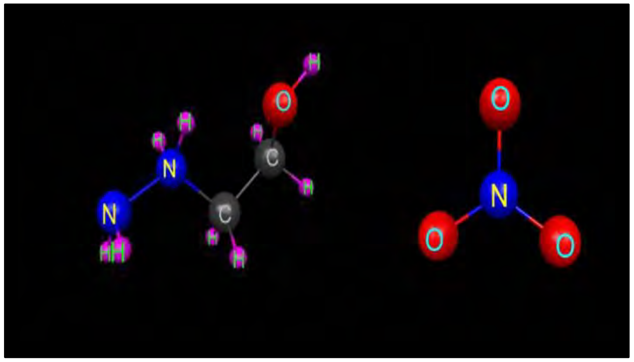
$$[THTDP]^+ [BH_4]^- + Al(BH_4)_3$$
$$\downarrow$$
$$[THTDP]^+ [Al(BH_4)_4]^-$$

Fuel\Oxidizer	90%H_2O_2	98%H_2O_2	N_2O_4	WFNA
$R_4P\ Al(BH_4)_4$ Ignition Delay	Ignition < 30ms	Ignition < 30ms	Ignition Vapor ignition	Explosive Rxn -

* Stefan Schneider, Tom Hawkins, Yonis Ahmed, Michael Rosander, Jeff Mills and Leslie Hudgens , *Angew. Chem. Int. Ed.* 12 May 2011, DOI: 10.1002/anie.201101752

Ionic Liquids as Explosives

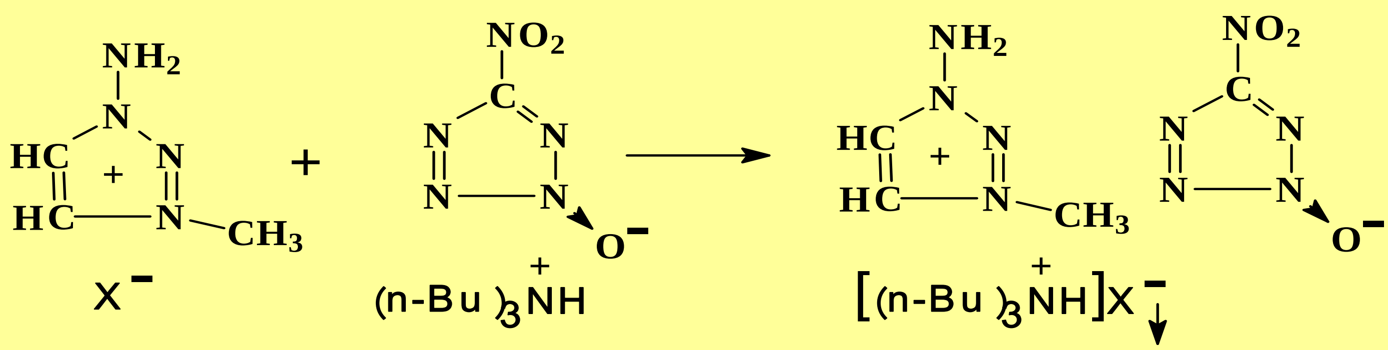




HEHN-Based Explosive DetonabilityTest (2-kg)

- **Initial USAF work on energetic RTILs over 15-years ago**
- **Recognized potential for advanced explosives**
- **Navy encouraged R&D on melt cast explosives**

IL-Based Explosive Properties



-AMT-ONT from metathesis rxn

-<u>Performance > TNT</u>

*J. C. Bottaro, M. A. Petrie, P. E. Penwell, NANO/HEDM Technology: Late Stage Exploratory Effort, Contract Number: F49620-02-C-0030, Final Report October 2003 (Public Release).

Ingredients	Heat of Formation (Kcal/mol)	Density (g/cc)	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/ms)	C-J Pressure (GPa)
AMT-ONT	+140 (est)	1.58	8.30	7.91	23.9
1-AMTN*	+17 (est)	1.63	7.92	8.12	23.6
TNT	-15 (exp)[5]	1.65	6.94	7.06	19.7

* T. Hawkins, G. Drake and A. Brand, US Patent 7,645,883, Jan 12, 2010.

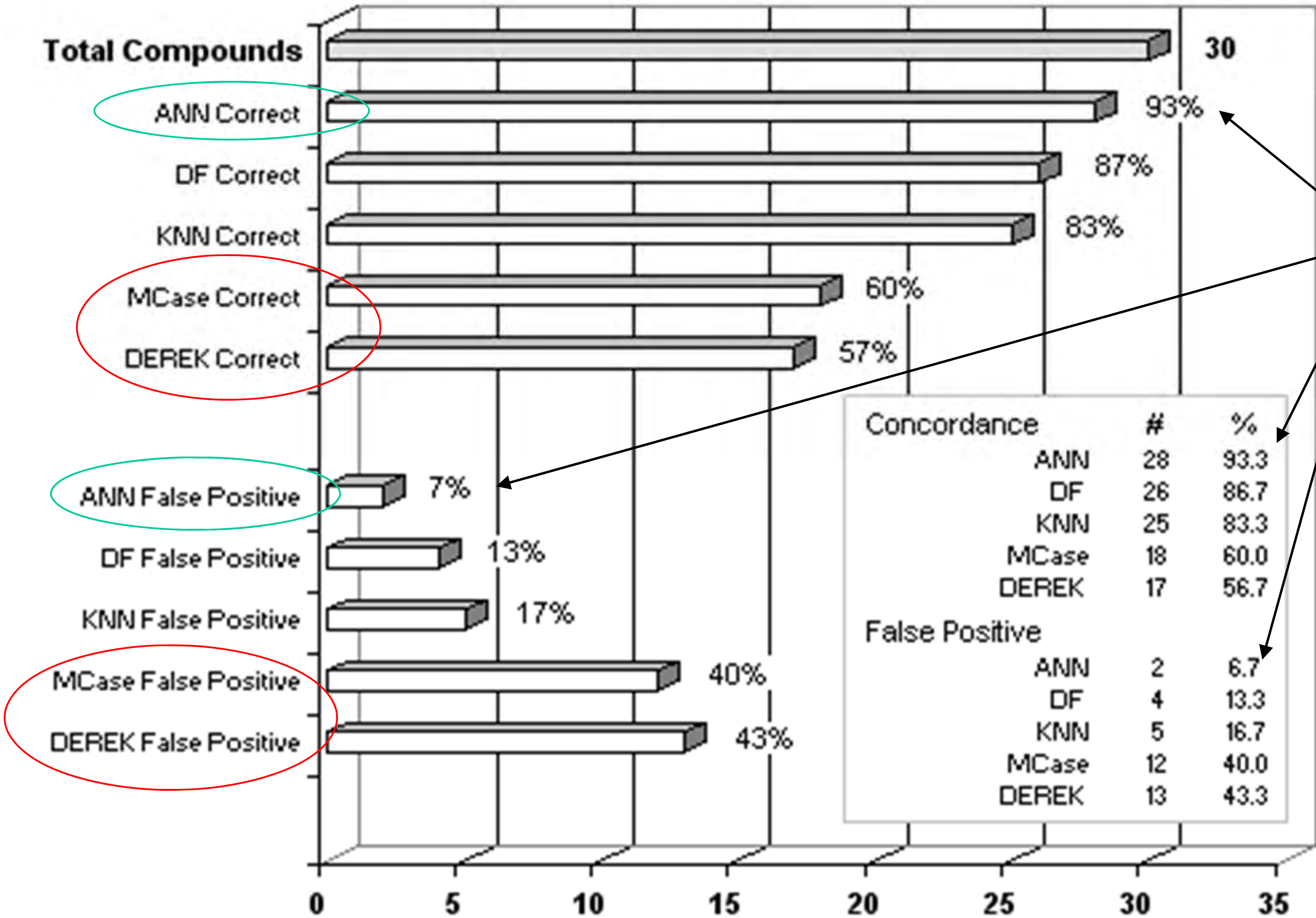
Another Challenge: Predictive Toxicology

- **Background**
  - **<u>Next generation propellants & explosives are emerging</u> with many programs championed by US Army, Navy and USAF involvement**
    - **Environmentally benign impact initiated devices (DOE)**
    - **Lead-free electrical & percussion primers (Navy/Army)**
    - **Chlorine-free pyrotechnics (Navy)**
    - **Chlorine-free (AP-free) solid propellant (Army/Navy/AF)**
  - **USAF AF-M315E**
    - **Propellant uses ionic liquids to yield low vapor toxicity**
  - **Sweden/ECAPS LMP-103S**
    - **Propellant uses ADN-based formulation**

New PEP materials are likely to employ advanced energetic molecules

***<u>Issue</u>*: Currently available, predictive toxicology models (e.g. TopKat, EPI Suite, ADMET) do not comprehensively handle EMs, particularly salts**

Comparison of prediction methods for general toxicity of 30 drugs in external test set

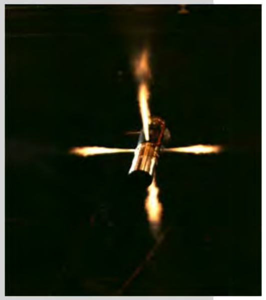


Artificial neural networks outperformed other methods

(Golbraikh, A. & Tropsha A., *J. Mol. Graphics Mod*. 2002, 20, 269-276.)

Predictive Methods Expected Payoff

- **Well-functioning, predictive toxicological methods for EM development can significantly affect life cycle costs for new systems**
- **DoD will be able to make more informed program decisions**
- **ESOH risks will be mitigated early in Acquisition/RDT&E process**



- **DoD will save $$$ in clean-up, compliance and restoration costs**

Summary

- **AFRL continues efforts in energetic ionic liquids research**
  - **IL-based propellants can convey unique capabilities**
  - **Energetic ILs have intriguing explosive properties**
- **IL material properties promise *significantly improved performance* & *reduced toxicity* compared to hydrazine fuels**
  - **Moving to lower testing/operations costs, improved operational responsiveness (as propellant candidates emerge, cost analysis will determine overall system benefits)**
  - **Leading to next generation systems with increased payload, range, and lifetime**

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– Cliff Bedford, ONR, Energetic ILs for Melt Castable Explosives